

Nature of Transients in the Laser Flash Photolysis of the Tribromocuprate(I) Complex

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Laser flash excitation of the CTTS band of CuBr_3^{2-} at 266 nm results in the formation of a luminescent species which decays through a coupled mechanism consistent with the formation of an emitting triplet tricoordinated exciplex in equilibrium with a nonemitting triplet dicoordinated species. The rate constants for some of the decay processes, as well as the formation constant of the radiative intermediate, are estimated. Hydrated electrons and Cu(II) ions are also efficiently produced in about a 1:1 molar ratio in a competing pathway with the copper(I) exciplex formation. Time-resolved absorbance spectra of the hydrated electron and the luminescent species were obtained, leading to the conclusion that the exciplex forms in high yield at high ligand concentrations. Another intermediate appears to be the Br_2^- radical anion.

Introduction

Over the past two decades, considerable effort has been expended trying to understand the details of the photochemistry of copper(I) complexes in solution.¹ Early studies revealed that equilibrated mixtures of CuCl_2^- and CuCl_3^- , or of CuBr_2^- and CuBr_3^{2-} very efficiently produce hydrated electrons when their CTTS bands, in the 270–280-nm region, are excited.^{2–7} This same kind of behavior was later observed in cyanocuprate(I),⁸ triamminecopper(I),^{9,10} and iodocuprate(I)^{11,12} and, recently, in mixed-ligand dicyanohalocuprate(I) complexes.^{13–15} Luminescence has also been observed in CTTS excitation of the chlorocuprate system at high ionic strength and high ligand concentration,¹⁶ and this behavior was subsequently observed in the bromocuprate(I),⁷ iodocuprate(I),¹¹ and mixed-ligand dicyanohalocuprate complexes¹³ as well but not in the cationic amminecopper(I) system.¹⁰ The dicyanohalocuprate complexes

have served as model systems for studying the nature of the luminescence,^{15,17,18} and it is now apparent that the emitting state is a tricoordinated exciplex, probably a triplet species, in near equilibrium with a nonemitting dicoordinated excited species, both of which decay through a coupled mechanism as shown in Scheme 1, where k_{PD} , k_{EL} , and k_{ED} represent radiationless deactivation of the dicoordinated precursor excited state back to the dicoordinated ground state, luminescent deactivation of the exciplex, and radiationless deactivation of the exciplex back to the tricoordinated ground state, respectively, X represents the CN ligand, and Y is Cl, Br, or I. The mixed-ligand exciplex also is quenched by reaction with halo ligands to form unspecified products, necessitating the introduction of a bimolecular rate constant, k_{ER} . The purpose of this study was to ascertain that the pure bromocuprate(I) complexes (in which X and Y both represent Br) essentially conform to this luminescence mechanism and to gain a clearer understanding of the relationship among the exciplex, the hydrated electron, and other short-lived transients formed following absorption of the UV laser pulse by these complexes.

Experimental Section

Stock solutions were prepared from reagent grade sodium bromide, lithium bromide, hydrobromic acid, or sodium perchlorate and standardized by density. The last solution was sintered-glass-filtered to remove any suspended matter which might exhibit luminescence, and all stock solutions were ascertained to have no background luminescence. Copper(I) was added to a solution of proper bromide ion concentration and ionic strength in the form of either CuCl or CuBr, prepared and purified as described previously,^{2,19} yielding solutions which were on the order of 10^{-4} M in copper(I) after a 2-fold dilution. All solutions were bubble-degassed with argon before being irradiated by the laser pulse, and in nearly all flash photolysis experiments a flow-

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- (1) Horváth, O. *Coord. Chem. Rev.* **1994**, *135/136*, 303.
- (2) Davis, D. D.; Stevenson, K. L.; Davis, C. R. *J. Am. Chem. Soc.* **1978**, *100*, 5344.
- (3) Davis, C. R.; Stevenson, K. L. *Inorg. Chem.* **1982**, *21*, 2514.
- (4) Kurtz, K. S.; Stevenson, K. L. *Proc. Indiana Acad. Sci.* **1985**, *94*, 187.
- (5) Horváth, O.; Papp, S. J. *Photochem.* **1985**, *30*, 47.
- (6) Horváth, O.; Papp, S. J. *Photochem.* **1985**, *31*, 211.
- (7) Stevenson, K. L.; Berger, R. M.; Grush, M. M.; Stayanoff, J. C.; Horváth, A.; Horváth, O. *J. Photochem. Photobiol., A* **1991**, *60*, 215.
- (8) Horváth, A.; Papp, S.; Décsy, Z. *J. Photochem.* **1984**, *24*, 331.
- (9) Stevenson, K. L.; Kaehr, D. M.; Davis, D. D.; Davis, C. R. *Inorg. Chem.* **1980**, *19*, 781.
- (10) Horváth, O.; Stevenson, K. L. *Inorg. Chem.* **1989**, *28*, 2548.
- (11) Horváth, O.; Fendler, J. H.; Stevenson, K. L. *Inorg. Chem.* **1993**, *32*, 227.
- (12) Horváth, O.; Fendler, J. H. *J. Photochem. Photobiol., A Chem.* **1993**, *71*, 33.
- (13) Horváth, A.; Stevenson, K. L. *Inorg. Chim. Acta* **1991**, *186*, 61.
- (14) Horváth, A.; Horváth, O.; Stevenson, K. L. *J. Photochem. Photobiol., A Chem.* **1992**, *68*, 155.
- (15) Horváth, A.; Stevenson, K. L. *Inorg. Chem.* **1993**, *32*, 2225.
- (16) Stevenson, K. L.; Braun, J. L.; Davis, D. D.; Kurtz, K. S.; Sparks, R. I. *Inorg. Chem.* **1988**, *27*, 3472.

- (17) Horváth, A.; Wood, C. E.; Stevenson, K. L. *J. Phys. Chem.* **1994**, *98*, 6490.
- (18) Horváth, A.; Wood, C. E.; Stevenson, K. L. *Inorg. Chem.* **1994**, *33*, 5351.
- (19) Stevenson, K. L.; Grush, M. M.; Kurtz, K. S. *Inorg. Chem.* **1990**, *29*, 3150.

Scheme 1

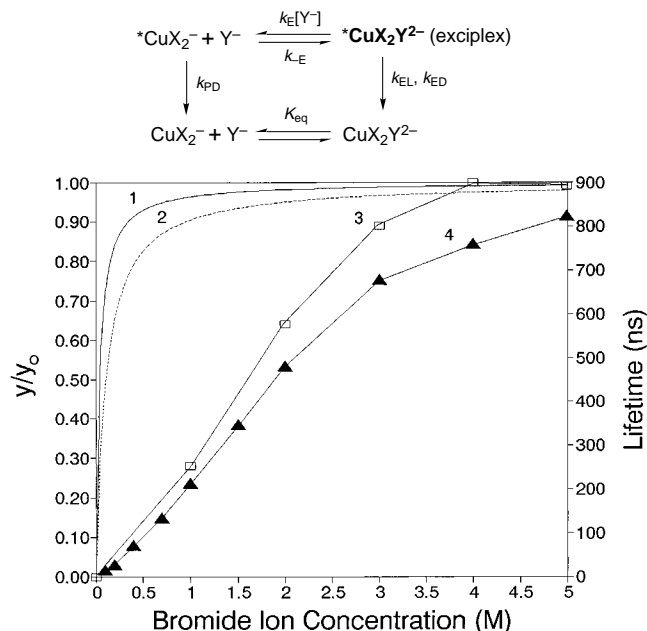


Figure 1. (1) Fraction of light absorbed by CuBr_3^{2-} and (2) mole fraction of copper which is CuBr_3^{2-} in solutions of CuBr containing Br^- at 5 M ionic strength (calculated from ref 21). (3) Relative luminescence emission intensity at 480 nm in solutions containing ca 1.6×10^{-4} M CuBr adjusted to constant optical density of 0.70 at the excitation wavelength of 266 nm, 5 M ionic strength, 298 K. (4) Emission lifetime (ns) in solutions of 10^{-4} M CuBr in 5 M ionic strength medium, 298 K.

through quartz cuvette (Hellma) was used in order to avoid successive exposures of the solution to the 266-nm laser pulse. The Nd-YAG laser systems used were recently described.¹⁷

The bromide ion activities in the various solutions of NaBr in 5 or 8.5 M constant ionic strength (NaClO_4 medium) were determined by measuring emf's of a Br^- -specific ion electrode (Orion) vs SCE and comparing to emf's in pure aqueous solutions of NaBr , for which the activities are given.²⁰

Results and Discussion

Luminescence. Under the conditions of these experiments, i.e. very low copper and rather high bromide concentrations, there is only one predominant copper(I) species in the ground state, namely CuBr_3^{2-} , in equilibrium with traces of CuBr_2^- .¹⁹ As described previously,⁷ this species emits a band centered at 475–480 nm when irradiated in its CTTS absorption band centered at 278–280 nm. Figure 1 shows how the relative intensity of the emission, excited at the laser wavelength of 266 nm, varies with the molar concentration of bromide ion at constant ionic strength. For comparison, the fraction of light absorbed by CuBr_3^{2-} and the fraction of copper in the form of CuBr_3^{2-} ¹⁹ are plotted in the same figure indicating that the rise in luminescence with bromide concentration is a result of some process other than a simple shifting of the ground-state equilibrium from CuBr_2^- to CuBr_3^{2-} .

The emission always follows a first-order decay in the nanosecond time domain with a lifetime that is rather sensitive to ligand concentration at constant ionic strength, increasing with increasing Br^- concentration, also shown in Figure 1, in a fashion very closely matching the emission intensity behavior. Such behavior bears some resemblance to that observed in the mixed-ligand halodicyanocuprate(I) model systems, where the decay is well-described by Scheme 1. In those systems, because

of the high degree of curvature and the existence of measurable y-intercepts in the plots of lifetime or quantum yield (arising from luminescence intensity) vs ligand concentration, it was possible to calculate nearly all of the various rate constants of Scheme 1, using a modified Marquardt fitting procedure²¹ applied to the expressions for dependence of quantum yield¹⁷ and lifetime²² on ligand concentration derived for such a coupled system. For the bromocuprate(I) system, on the other hand, the plots of Figure 1 are somewhat less informative, yet it is still possible to show that the exciplex kinetic model is consistent with the observed behavior and that some kinetic parameters can be calculated or estimated.

The simplest analysis assumes that the two excited-state species in Scheme 1 are very close to equilibrium during the decay process; i.e., k_E and $k_{-E}[Y^-]$ are much larger than k_{PD} and $k_{EL} + k_{ED}$, so that both excited species decay at the same rate. It is also not necessary to assume that there is a reaction of the exciplex with the ligand (k_{ER}). The kinetics for such a system in the equilibrium limit has been well-described by McMillin et al.²³ and yields for our system the expression for the lifetime

$$\tau = \frac{k_{-E} + k_E[Y^-]}{k_{PD}k_{-E} + k_D k_E[Y^-]} \quad (1)$$

where $k_D = k_{EL} + k_{ED}$. Noting that the observed rate constant, k_{obs} , is the reciprocal of the lifetime, and by rearranging, one can obtain the expression

$$k_{obs} = k_D + \frac{k_{PD} - k_D}{1 + K_{ex}[Y^-]} \quad (2)$$

where the excited-state equilibrium constant, K_{ex} , is given by k_E/k_{-E} . It is thus possible to find the value of K_{ex} which gives the best linear fit of the values of k_{obs} versus $1/(1 + K_{ex}[Y^-])$. From the slope and intercept of such a plot, the values of k_D and k_{PD} can then be determined. This was done for the lifetime data of Figure 1, but activities rather than concentrations were used because of the wide variations of concentration and very high ionic strength. The resulting plot utilizing the optimum value of K_{ex} is shown in Figure 2. Table 1 shows the resulting rate constants and equilibrium constant for exciplex formation, which is about one order of magnitude greater than that for the ground-state equilibrium, where $K_{eq} = 9.5$,¹⁹ a behavior also seen in the mixed-ligand halodicyanocuprate(I) complexes.¹⁷

The luminescence lifetime in the chlorocuprate(I) system was previously shown to increase with ionic strength,¹⁶ and this has been observed in the bromocuprate(I) system, where increasing the ionic strength of solutions of CuBr from 5 to 8.5 M caused about a 4-fold increase in luminescence lifetimes. Measurements of lifetime-vs-bromide ion concentration were obtained, and a plot of the data, in the form of decay constant vs $1/(1 + K_{ex}a_{Br^-})$, is shown in the inset of Figure 2. Rate and equilibrium constants obtained from these plots are shown in Table 1 so that the effects of the ionic media can be compared. The most dramatic difference is that the slope of the plot at 8.5 M is quite a bit smaller than that at 5 M ionic strength (0.0052 vs 0.266 ns^{-1}), which causes a 50-fold decrease in the value of k_{PD} . This demonstrates how important this pathway is in the decay of the luminescent exciplex, and since it appears to be a

(21) Marquardt, D. W. *J. Soc. Ind. Appl. Math.* **1963**, *11*, 431.

(22) Demas J. N. *Excited State Lifetime Measurements*; Academic Press: New York, 1983; pp 59, 240–242.

(23) Kirchoff, J. R.; Gamache, R. E., Jr.; Blaskie, M. W.; Del Paggio, A. A.; Lengel, R. K.; McMillin, D. R. *Inorg. Chem.* **1983**, *22*, 2380.

(20) Hamer, W. J.; Yung-Chi, W. *J. Phys. Chem. Ref. Data* **1972**, *1*, 1067.

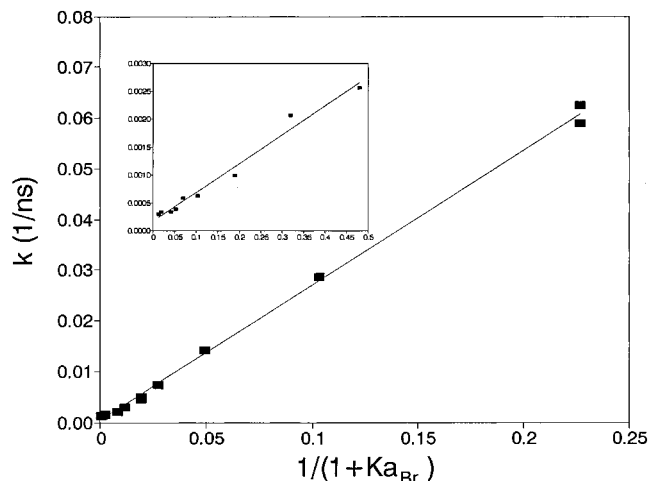


Figure 2. Luminescence emission decay constant at 480 nm vs $1/(1 + K_{ex}a_{Br})$ (K_{ex} determined by best linear fit given by correlation coefficient) in solutions containing 10^{-4} M CuBr, NaClO₄, and NaBr at a constant ionic strength of 5.0 M. Inset: a similar type of plot for 8.5 M ionic strength solutions.

Table 1. Estimated Rate and Equilibrium Constants for the Decay of Luminescence (Scheme 1) of CuBr₃²⁻ in Solutions of 5 and 8.5 M Ionic Strengths

pathway	rate constant	
	5 M ionic str	8.5 M ionic str
$10^{-5}k_D$ (s ⁻¹) (= $k_{EL} + k_{ED}$)	4.0	1.7
$10^{-7}k_{PD}$ (s ⁻¹)	27	0.53
$K_{EX} = k_E/k_{-E}$	73	7
K_{eq} (ground-state equil)	9.5 ^a	

^a From ref 19.

route limited only to nonradiative deactivation processes, it is easy to see how increasing the rigidity of the solvent medium by extending the ionic strength nearly to the solubility limit slows down the vibrational transfer of energy, drastically reducing the rate.

Transient Absorbance. Several different absorbing species are formed immediately following absorption of the laser flash by these systems. Figure 3 shows the transient spectra at various delay times following the flash for a 10^{-4} M solution of CuBr in neutral 5 M NaBr, along with the absorption band of the tribromocuprate(I) ion. These transient spectra were attributed to absorption and reaction by the copper(I) species rather than Br⁻ since (1) flash irradiations of pure NaBr yield time-resolved spectra with bands that are about one-seventh as intense at 360–400 nm and one-third as intense at 700 nm as those observed for the bromocuprate solutions in 5 M NaBr, and (2) the absorbance of the copper complexes at the laser output of 266 nm is more than 10 times that of 5 M NaBr, which has an extinction coefficient considerably less than 1 at 266 nm, meaning that at this wavelength the copper complex absorbs more than 90% of the light. A power study also indicated that the concentrations the transients are proportional to laser intensity, indicating that these processes are monophotonic. Some of the prominent features and changes in the spectra which occur during the 4500-ns time span are (1) a strong bleaching at about 280 nm, giving a negative change in absorbance which does not decay significantly during this time regime, (2) an absorption band peaking at 360 nm which is not quite completely decayed by the end of the span, and (3) a wide band centered at 720 nm which completely decays during the time span.

The bleaching at 280 nm and the band formed at 720 nm

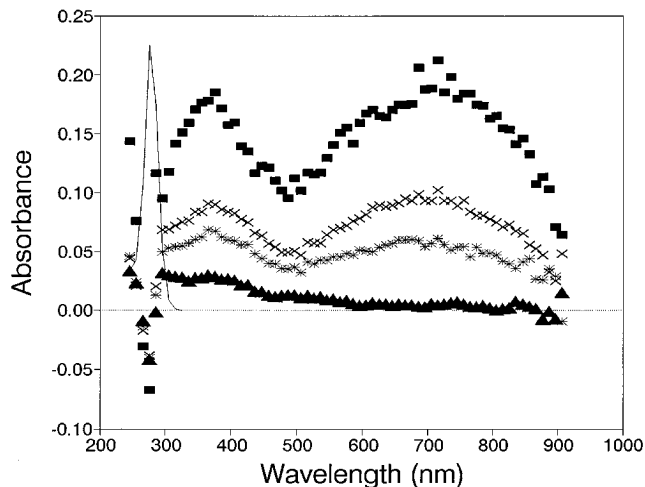
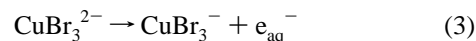


Figure 3. Transient absorbance spectra of 1.0×10^{-4} M CuBr in 5.0 M NaBr at delay times of (■) 50, (×) 500, (*) 1000, and (▲) 4400 ns after excitation by the 266-nm laser pulse, 1-cm quartz cuvette, 298 K. The absorption band of the photoactive CuBr₃²⁻ species is shown (—) at one-fourth its absorbance values in the irradiated sample.

can be attributed to the decomposition of CuBr₃²⁻ and the formation of the hydrated electron, respectively, after absorption of the laser pulse. A dominant reaction is probably oxidation of the bromocuprate(I) species,



This is seen from the fact that since CuBr₃²⁻, CuBr₃⁻, and e_{aq}⁻ have molar extinctions of about 9500,¹⁹ 1500²⁴ (both at 280 nm), and 18 000²⁵ (at 720 nm), respectively, and if one extrapolates the 360-nm band into the region where the bleaching occurs, then the stoichiometric ratio of CuBr₃²⁻ decomposed to e_{aq}⁻ formed is close to 1:1, an observation that is consistent with earlier observations.⁷ Moreover, the faster decay of the electron compared to that of the nascent copper(II) species demonstrates the previously-observed¹⁴ very efficient electron scavenging by ground-state copper(I).

The absorption band in the 360–400-nm region is somewhat more enigmatic. The radical anion, Br₂⁻, is known to have an absorption maximum at about 360–370 nm with an absorption coefficient of about 10 000.²⁶ However, there are several reasons that there must be some species other than Br₂⁻ to account fully for this band. First, the band in Figure 3 is almost as high as that of the hydrated electron, which would suggest that about two Br₂⁻ radicals would have to form for each hydrated electron. Second, the appearance of this band is strongly dependent on ligand concentration. Figure 4 compares the time-resolved spectra, taken at 100 ns after the flash, of several flashed solutions of 10^{-4} M CuBr, where the intensities of the absorbed laser pulses are about the same. Comparison of the spectra of neutral solutions of 5 and 1 M NaBr indicates that the 360–400-nm band all but disappears in the low ligand concentration solution whereas the band of the hydrated electron and the bleaching caused by photodecomposition of CuBr₃²⁻ are about the same. The figure also shows that, in an acidic (pH = 2) solution of 5 M NaBr, the hydrated electron band disappears, whereas the bleaching is unchanged and the 360-nm band is partly reduced. This can be explained by the fact that at this pH, the electron is completely scavenged in 100 ns,

(24) Unpublished results.

(25) Michael, B. D.; Hart, E. J.; Schmidt, K. H. *J. Phys. Chem.* **1971**, *75*, 2798.

(26) Zehavi, D.; Rabani, J. *J. Phys. Chem.* **1972**, *76*, 312.

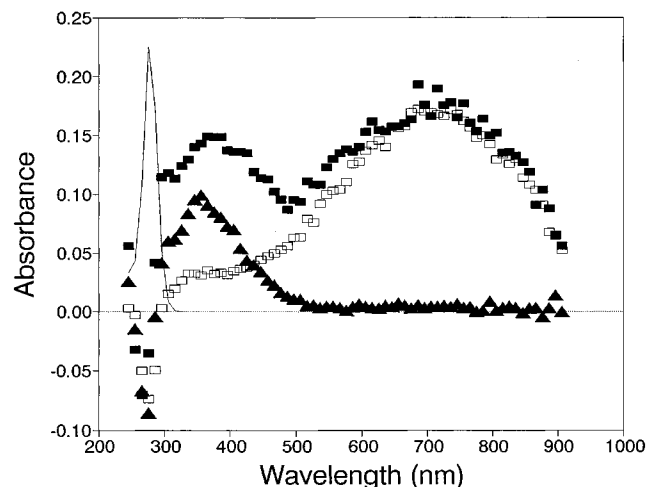


Figure 4. Transient absorbance spectra 100 ns after absorption of the 266-nm laser pulse for solutions of 1.0×10^{-4} M CuBr in (■) neutral, 5 M NaBr, (□) neutral, 1 M NaBr, and (▲) 5 M NaBr at pH = 2. The absorption band of the photoactive CuBr_3^{2-} species is shown (—) at one-fourth its absorbance values in the irradiated sample.

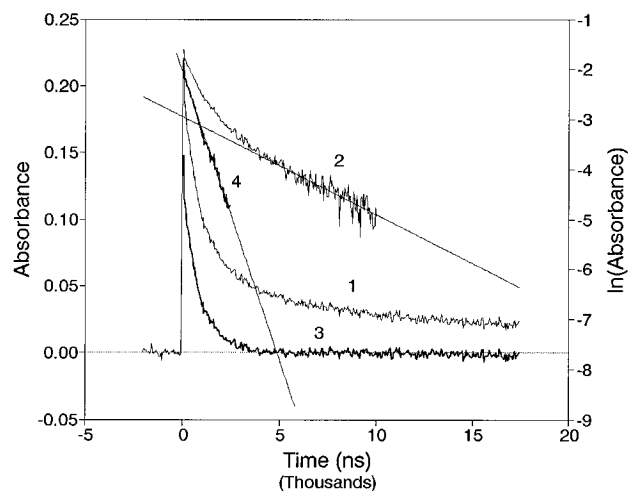


Figure 5. (1) Absorbance decay signal at 390 nm for a solution of 8.7×10^{-5} M CuBr in neutral, 5 M NaBr, after excitation by the 266-nm laser pulse, in a collinear laser/analyzing beam arrangement. (2) Logarithmic plot of data in (1), with a linear regression fit to data between 5000 and 10 000 ns. (3) Resolved decay signal of fast-decaying species. (4) Logarithmic plot and linear regression fit of fast-decaying signal.

whereas if the 360–400-nm band can be ascribed to the luminescent exciplex, the latter will be only partially quenched during this time span due to the difference in hydronium ion quenching constants ($5.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for e_{aq}^- vs $6.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ for the luminescent species).⁷ This does not rule out Br_2^- at this point because this species would not be expected to react with the hydronium ion either.

The kinetic evidence, however, clarifies the situation. There are apparently two species which exhibit absorbance decays in the 300–400-nm range, as indicated by the biexponential absorbance decay behavior shown in Figure 5. The two rate constants or lifetimes for such decays were obtained by component-stripping,²⁷ and the short-lived decay as well as the slopes for the two logarithmic plots are also shown in Figure 5. The fast and slow decay lifetimes were measured under a variety of conditions and compared to the luminescence lifetimes under the same conditions, and it was seen that there is a good

Table 2. Comparison of Lifetimes of Fast Absorbance Decay in the 300–450-nm Region with Emission Decay at 480 nm for the Bromocuprate(I) System under a Variety of Solvent Conditions ($[\text{CuBr}] = 10^{-4} \text{ M}$)

solvent system			lifetime ^a (ns)	
[NaBr] (M)	pH	ionic str (M)	absorbance (λ , (nm))	emission at 480 nm
5	7	5	789 (360)	814
5	3	5	495 (330)	548
3	7	3	92 (330)	100
2	7	2	29 (360)	33

^a Error limits on absorbance lifetimes and luminescence lifetimes are $\pm 20\%$ and $\pm 10\%$, respectively.

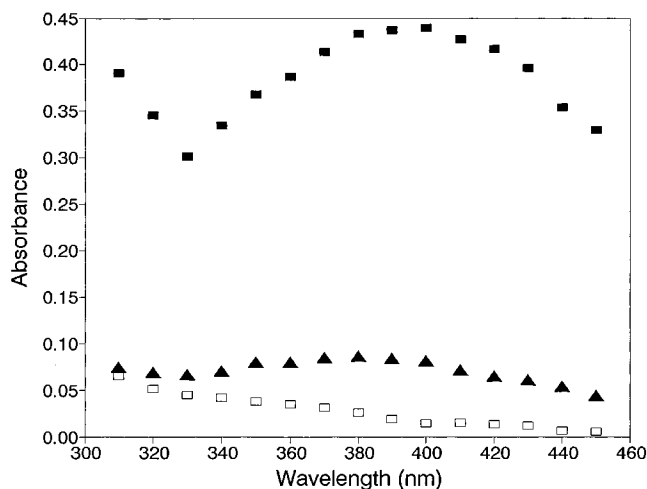
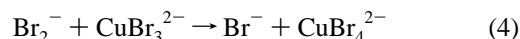


Figure 6. Time-resolved absorbance spectra of components of 1.7×10^{-4} M CuBr in neutral 5 M NaBr solution, taken in a collinear laser/analyzing beam arrangement: (■) fast-decaying (exciplex) species extrapolated to $t = 0$ ($\lambda_{\text{max}} = 390\text{--}400 \text{ nm}$); (▲): slow-decaying species taken $4.5 \mu\text{s}$ after pulse ($\lambda_{\text{max}} = 380 \text{ nm}$); (□): long-time absorbance taken $45 \mu\text{s}$ after pulse.

correlation between the fast absorbance decay and luminescence, as indicated by the representative data of Table 2. It is reasonable, then, to identify this absorbance as that of the emitting exciplex species.

A higher resolution absorption spectrum of the exciplex species, which we identify as a triplet excited state, can be obtained by calculating the zero-time absorbance values of the fast-decaying species for a series of transient decays, like those in Figure 5, at different wavelengths in an experimental setup in which the analyzing and laser beams share identical collinear paths in the cuvette, resulting in much stronger absorbance signals. This was done for the wavelength range, 310–450 nm, and the results are shown in Figure 6. This band has a peak at about 400 nm, a somewhat longer wavelength than is expected for Br_2^- .²⁶

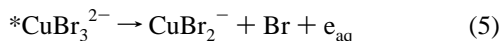
The slow-decaying absorber of Figure 5 is probably Br_2^- since its decay was found to be relatively insensitive to ligand concentration and pH. The resolution procedure gave an absorption band, taken at $4.5 \mu\text{s}$ after the pulse and also shown in Figure 6, with a maximum absorption at about 370–380 nm corresponding to that of Br_2^- . A likely pseudo-first-order decay pathway open to Br_2^- would be a bimolecular redox atom-transfer reaction with ground-state copper(I)



From the average first-order decay lifetime of this species of 4500 ns and the copper(I) concentration of 10^{-4} M , we can estimate a second-order rate constant of $2.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.

(27) Demas J. N. *Excited State Lifetime Measurements*; Academic Press: New York, 1983; p 40.

The main source of Br_2^- is probably the ejection of an electron from a ligand rather than a copper(I) atom in the initially excited CuBr_3^{2-} species (eq 5), as suggested by the time-resolved spectrum of 1 M NaBr (which does not luminesce measurably) in Figure 4, followed by rapid combination of Br^\bullet and Br^- to



form the dibromide radical. This could account for the relatively large 360-nm band in Figure 3 even after 1000 ns (greater than 1 lifetime in the decay of the luminescent species) had elapsed.

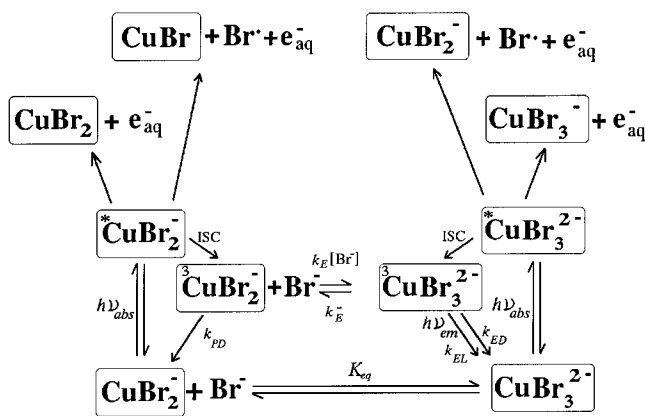
The decay of the longer-lived species (curve 1 in Figure 5) gives a nonzero infinite-time value for absorbance, probably corresponding to the copper(0) species formed by scavenging of the hydrated electron by copper(I). The time-resolved spectrum of this species is shown as curve 3 of Figure 6, yielding a broad absorbance which gradually increases from the visible region into the UV, consistent with scattering caused by microprecipitation of the copper(0) species.

The intensity of the fast-decaying exciplex absorption suggests that this band is a spin- and symmetry-allowed transition and that the exciplex is formed at rather high quantum yield, essentially by intersystem crossing from the excited tribromocuprate complex, $*\text{CuBr}_3^{2-}$. If we assume that the extinction coefficient of this species is equal to or less than that of the hydrated electron (i.e. $18\,000\text{ M}^{-1}\text{ cm}^{-1}$), and noting that the peak heights at 360–400 and 700 nm in Figure 4 are about the same immediately following absorption of the pulse with two thirds of the 360–400-nm peak attributed to the fast-decaying species (see above), we must conclude that the exciplex concentration is about equal to or greater than about two-thirds of that of the hydrated electron. Our earlier results⁷ indicated that hydrated electrons are formed in these solutions, as in eq 3, with a quantum efficiency of 0.21; thus, the minimum quantum yield of exciplex formation would have to be 0.14. This leads us to the conclusion, then, that the exciplex is formed very efficiently in high ligand concentrations.

If the slow-decaying species is indeed Br_2^- and its initial concentration contributes to about one-third of the absorbance of the 360–400-nm band in Figure 4, then from its extinction coefficient²⁶ we can estimate that its quantum yield of formation must be about 0.12.

Thus it is apparent that about half the excited copper(I) species decays through reactive pathways, which may be oxidative or reductive or may proceed via intersystem crossing to the luminescent exciplex. Scheme 2 summarizes these various pathways following the flash photolysis of bromocuprate(I). At

Scheme 2



the bottom right of the scheme, the photoactive species, CuBr_3^{2-} , is excited by the UV absorption to an excited state, $*\text{CuBr}_3^{2-}$, previously described as a CTTS state.⁷ Four fast-decay pathways are open to this state: (1) radiationless decay back to the ground state, (2) ejection of an electron and formation of the Cu(II) species, CuBr_3^- , (3) ejection of an electron and formation of Br_2^\bullet and the copper(I) species, CuBr_2^- , and (4) intersystem crossing to the triplet species, $^3\text{CuBr}_3^{2-}$, which we identify as an exciplex because it rapidly establishes an equilibrium with the ligand, Br^- , and another triplet, $^3\text{CuBr}_2^-$. The exciplex has at least three decay pathways available to it: (1) emission (k_{em}) and (2) radiationless decay (k_{ED}) to the ground state and (3) rapid equilibration causing ejection of Br^- , forming the nonemitting triplet, $^3\text{CuBr}_2^-$, whose decay back to ground-state dibromocuprate(I) (with rate constant k_{PD}) may be the most important factor in determining the lifetime of the exciplex. Although nearly all of the studies reported in this paper occurred in solutions in which the predominant photoactive species was CuBr_3^{2-} , we have shown previously that CuBr_2^- can also be excited to a CTTS state which ejects electrons presumably by the same routes available to $*\text{CuBr}_3^{2-}$. We also make the assumption that this excited state can decay to the nonemitting triplet through intersystem crossing.

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